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Coating Microstructure-Property-Performance Issues

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COATING MICROSTRUCTURE-PROPERTY-PERFORMANCE ISSUES

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ABSTRACT

Results of studies on the relationships between spray parameters and performance of thermally-sprayed intermetallic coatings for high-temperature oxidation and corrosion resistance are presented. Coating performance is being assessed by corrosion testing of free-standing coatings, thermal cycling of coating substrates, and coating ductility measurement. Coating corrosion resistance was measured in a simulated coal combustion gas environment (N_2-CO-CO_2-H_2O-H_2S) at temperatures from 500 to 800°C using thermo-gravimetric analysis (TGA). TGA testing was also performed on a typical ferritic-martensitic steel, austenitic stainless steel, and a wrought Fe_3Al-based alloy for direct comparison to coating behavior. FeAl and Fe_3Al coatings showed corrosion rates slightly greater than that of wrought Fe_3Al, but markedly lower than the steels at all temperatures. The corrosion rates of the coatings were relatively independent of temperature. Thermal cycling was performed on coated 316SS and nickel alloy 600 substrates from room temperature to 800°C to assess the relative effects of coating microstructure, residual stress, and thermal expansion mismatch on coating cracking by thermal fatigue. Measurement of coating ductility was made by acoustic emission monitoring of coated 316SS tensile specimens during loading.

INTRODUCTION

The overall goal of research on thermal-spray coatings for high-temperature environmental resistance at the Idaho National Laboratory is to better understand the relationships between coating processes, coating characteristics, and coating performance. Towards these ends, the effects of coating process variables (primarily thermal spray particle temperature and velocity) on the characteristics of a number of different coating materials have been studied. These include iron aluminides formed by high-velocity oxy-fuel (HVOF) spraying and Mo-Si-B coatings formed by air plasma spraying (APS).[1-3] The coatings have been applied to variety of structural substrates: low-alloy ferritic steels, advanced ferritic-martensitic steels, austenitic stainless steels, and Ni-base alloys. A wide variety of coating characteristics have been determined: microstructure, thermal expansion, elastic modulus, hardness, and residual stress. The dependence of these characteristics on coating process parameters is reasonably well understood.

The next phase of research is to determine the influence of coating characteristics on performance. The purpose of coating performance testing is to establish a baseline of performance-related properties and characteristics sufficient to screen different coating types and processes and provide some level of confidence prior to service testing. Laboratory-based performance testing can also help determine the contributions of different coating system parameters to critical properties, enabling the selection of the ideal set of parameters for service testing and the assessment of the effects of variations from the ideal parameters. Service testing will ultimately be required, however, since it is nearly impossible to fully duplicate in a laboratory test the exact nature and range of conditions encountered in service. Reference [4] describes some of the complexities encountered in service which would be difficult to anticipate in a laboratory.

Laboratory-based coating performance tests used at the INL focus on two areas—environmental resistance and durability. Environmental resistance, the essential function of the coating, is clearly of prime importance. Coatings are typically created from feedstock materials which are known to be resistant to the specific environment of interest, but it still must be demonstrated that that material in coating form possesses similar resistance. It is also important to understand the effects of thermal cycling, which typically increases attack through spallation of protective oxides. Finally, for coatings the influence of stresses and strains imposed by the substrate on environmental resistance must be understood. These stresses may be residual from the coating process or may result from thermal expansion mismatch strains.

Environmental resistance is studied by performing several different tests. First, gas-phase corrosion testing using thermo-gravimetric analysis (TGA) is performed on free-standing coatings (i.e., with the substrate removed) to measure intrinsic coating behavior. Free-standing coatings may also be tested with combined gas and ash or slag corrodent. In this case tests are performed by long-term furnace exposure and metallographic examination of attack. For both cases tests are performed under both isothermal and cycling conditions. Finally, coated substrate test coupons are tested by furnace exposure and metallographic examination. Testing of this type is complicated by the possibility of accelerated attack of the substrate or exposed coating-substrate interfaces, depending on the test coupon configuration.

Coating durability testing is equally important, since the most environmentally-resistant coating will not protect the substrate if it has spalled off or been severely cracked. Laboratory characterization of coating durability is difficult again because of the difficulty in replicating the range of service conditions, but also because “durability” is not a unique property of the coating or the coating-substrate system which can be unambiguously measured. This problem is reflected in the wide variety of tests available for durability testing in the coating literature. Durability can be roughly broken into two aspects: adherence and cracking resistance. Adherence of coatings is commonly measured by the tensile adhesion test (TAT) according to the ASTM C 633 or other standard methods,[5] but the results obtained are dependent on the test method and do not provide a material or system property that can be used in design. The resistance of the coating-substrate interface to crack propagation, assessed using fracture toughness techniques, is a more fundamental measure of adhesion.[6] A range of test techniques are available for measuring this parameter, but it does not appear to be as widely applied as the TAT, likely due to the difficulty in performing the tests and the fact that the results are still difficult to apply in design conditions.

Resistance to cracking due to tensile loading prior to service is relatively straightforward to measure by simply loading coated substrates until cracking is noted. Coating fracture tests may be performed in tension or bending and

cracks may be detected by visual, metallographic, acoustic, or other means. It must be understood that fracture strains (or stresses) so measured are coating-substrate system properties and not necessarily intrinsic to the coating, since they depend on coating residual stresses, coating thickness, and other system characteristics. Determining the cracking behavior or coatings due to service conditions is more difficult, since this may involve creep, various forms of fatigue, environmental attack, or some combination of these. The coating-substrate thermal expansion mismatch can be a major contributor to service-related cracking. Thermal cycling of coated substrates is one way to characterize resistance to thermal fatigue cracking.

This paper presents the results of initial coating performance testing of the types described above; in particular TGA testing of free-standing coatings in a simulated coal combustion gas environment, thermal cycling tests of coated substrates, and room-temperature coating fracture testing. Testing was primarily performed on iron aluminide coatings (both FeAl and Fe_3Al) sprayed onto low-carbon or austenitic stainless steels at a range of spray particle velocities.

EXPERIMENTAL METHODS

TGA CORROSION TESTING

Corrosion tests were performed on free-standing iron aluminide coatings, a wrought Fe_3Al-based alloy, and typical substrate alloys. Fe_3Al and FeAl coatings were prepared by HVOF spraying onto stainless steel substrates at spray particle velocities of 560 and 620 m/s for Fe_3Al and 540 and 700 m/s for FeAl. Detailed coating procedures are given in Refs. [1] and [3]. Coatings roughly 1.5 mm thick were created from which free-standing rectangular coating TGA specimens $4 \times 4 \times 0.5$ mm^3 were machined. Similar-sized specimens were machined from wrought Fe_3Al sheet (alloy FAS with 2% Cr), Grade 91 steel bar (9Cr-1Mo-VNb), and type 316 stainless steel bar. Isothermal TGA tests were performed at 500, 600, 700, and 800°C for 25 hr and 100 hr durations in an environment of flowing (~200 ml/min) N_2-9%CO-4.5%CO_2-1.8%H_2O-0.12%H_2S. This is the mixed oxidizing-reducing environment used by Lehigh University [7] and Albany Research Center.[8] For this gas mixture the equilibrium oxygen and sulfur activities are reported as 10^{-19} and 10^{-8}, respectively. For all materials reaction rates typically decreased at the beginning of the tests, sometimes becoming linear at longer times. Consistent linear, parabolic, or paralinear behavior was not observed. For the purpose of material and temperature comparison the corrosion rates were characterized by a linear fit to the weight gain versus time curve near the end of the test. Metallography was performed on selected specimens to characterize the depth and nature of corrosion products formed.

THERMAL CYCLING TESTS

The thermal cycling resistance of several coating-substrate combinations was assessed by subjecting coated substrates to multiple thermal cycles consisting of heating to 800°C, holding at temperature for one hour, and slow furnace cooling. The coating materials tested were 316 SS, Fe_3Al, FeAl, and Mo-Si-B. Varied spray particle velocities were considered, and low-carbon steel, stainless steel, and Inconel alloy 600 substrates were used. The Mo-Si-B coatings were prepared by APS.[3] The coatings were approximately 500 μm thick and the substrates were cylindrical and approximately 25 mm in height and diameter. Coatings were applied to a flat surface. Post-test metallographic examination of cross-sections was performed to reveal coating cracking. Specimens were examined that had received 1, 15, and 30 cycles.

COATING FRACTURE STRAIN TESTING

The room-temperature fracture strain of Fe_3Al and FeAl coatings was measured by tensile testing coated substrates. The substrates were rectangular dogbone-shaped; coatings approximately 500 μm thick were applied to the reduced section. The gage cross-section of the substrates was 12.9 mm width × 6.5 mm thick and the gage length was 50 mm. Substrate strain was monitored using a clip-on extensometer; the coated substrates were pulled in tension until coating failure was indicated (typically to 1% strain). Coating cracking was monitored by two acoustic emission sensors attached to the substrate in the grip sections at both ends of the specimen (Fig. 1). The two sensors allowed

the Vallen Systeme AMSY4 acoustic emission acquisition and analysis system to locate events in the coated length and screen out unrelated noise. Coating cracking was clearly indicated by high-energy events in the coated section which corresponded to visually-observable cracks. No events in the gage section were noted prior to the high-energy events.

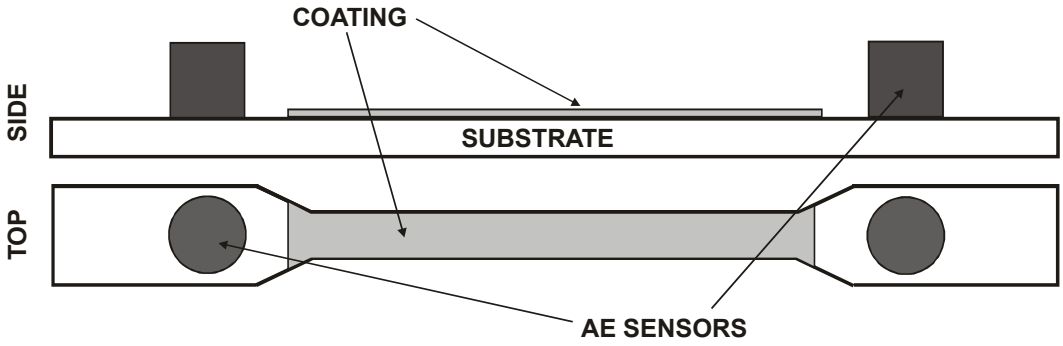
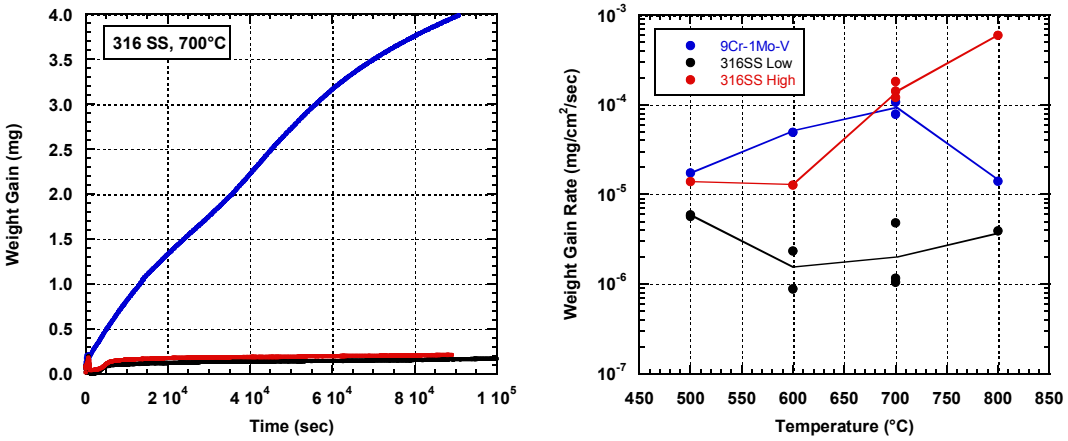


Figure 1: Schematic of coated tensile test specimen for coating fracture strain measurement.

RESULTS AND DISCUSSION

CORROSION TESTING

Corrosion rates of the steel substrate materials are illustrated in Figure 2. While consistent attack with a peak at 700°C was observed for the 9% Cr ferritic-martensitic steel, the type 316 stainless steel showed variable behavior, either severe or very little attack. Figure 2a shows weight gain curves for three different 316 SS specimens under identical conditions; the weight gain on two is essentially zero while the third shows a high rate. The high and low rate behaviors are indicated separately on Figure 2b, which shows the variation of linear end-of-test rates for both alloys as a function of temperature. The source of the highly variable behavior of 316 SS is currently unknown but being studied further. Metallographic examination of cross-sections of tested specimens show the primary corrosion products to be iron sulfide and iron-chromium oxides. Good correspondence was found between the weight gain and the metallographically-observed extent of attack.

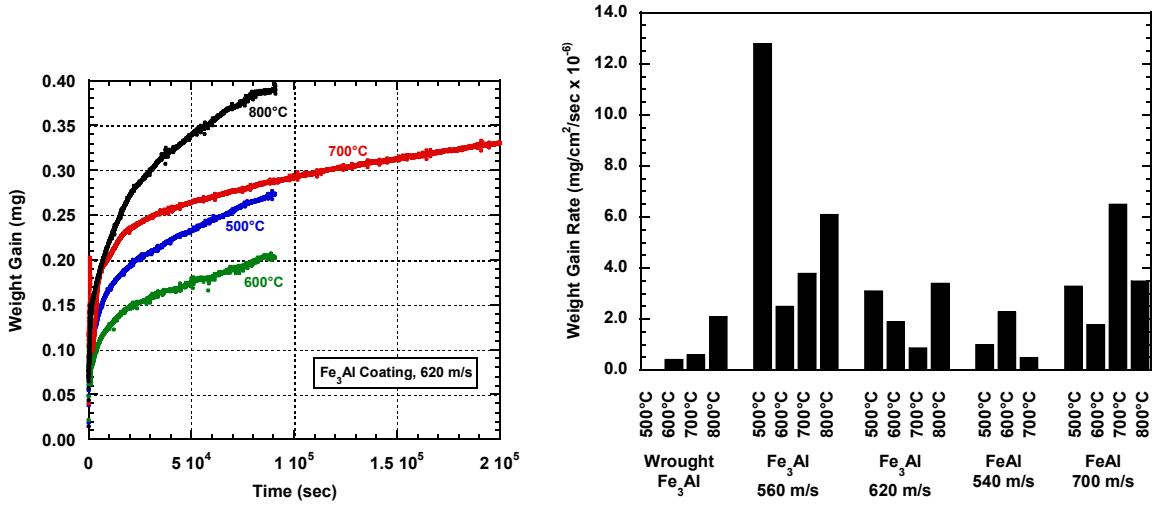


(a) (b)

Figure 2: (a) weight gain versus time for repeated runs on 316 SS, (b) weight gain rates as a function of temperature for grade 91 steel and 316 SS.

Figures 3a and 3b summarize the TGA results for wrought Fe_3Al and the coatings. The coatings all showed initially decreasing rates of weight gain which became linear at longer durations. The magnitude of weight gain was small but resolvable. As seen in both figures no consistent trends in end-of-test linear rate of attack with temperature, coating material, and coating spray particle velocity exist, but the oxidation rates of the coatings appear to be slightly greater than those of the wrought Fe_3Al alloy. As shown in Figure 4, little indication of attack has been observed in metallographic cross-sections of tested specimens, consistent with the low weight gains measured. Figure 5 compares corrosion rates of the various materials at a condition of 700°C and 100 hr duration. The markedly greater resistance of the coating materials than the 9Cr steel and the "high" rate of attack of the 316 SS is readily apparent. The "low" rate of attack of the 316 SS is actually lower than the coating corrosion rates, however.

The corrosion rates observed in this series of tests are approximately ten times lower than those reported for similar HVOF-sprayed Fe_3Al coatings reported by Corvino, et al.[8] Tests in the earlier work consisted of 160 hr furnace exposure of coated substrates with weighing before and after exposure. Two factors may explain the large differences in oxidation rates between the current and previous results—the presence of the substrate and the difference in coating microstructure. Stresses imposed by the substrate may accelerate corrosion rates, and the presence of the much higher fraction of unmelted particles in the coatings of the previous study appear to have led to coating cracking and attack along unmelted particle boundaries.



(a) (b)

Figure 3: (a) weight gain versus time curves for a Fe_3Al coating at different temperatures, (b) comparison of weight gain rates for coatings and wrought Fe_3Al as a function of temperature.

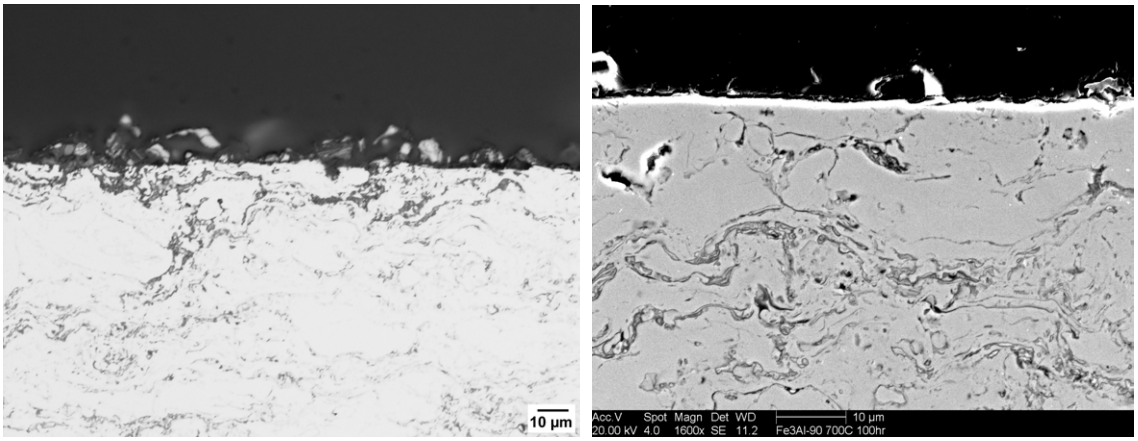


Figure 4: Metallographic cross-section of surface of Fe_3Al coating sprayed at 620 m/s after 100 hr, 700°C exposure to simulated coal combustion gas.

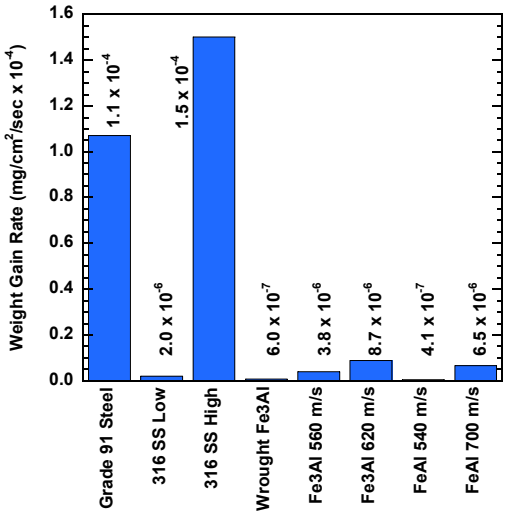


Figure 5: Comparison of corrosion rates for different materials at 700°C, 100 hr exposure.

THERMAL CYCLING TESTS

The results of thermal cycling tests on a number of different coating-substrate combinations are listed in Table 1, along with the results of a simple elastic analysis of the stress-strain development in the coatings resulting from the combination of initial residual stress and coating-substrate thermal mismatch strains. Initial residual coating stresses were estimated using deposition stresses derived from curved coating-substrate coupons using the Tsui-Clyne progressive deposition model.[9, 10] They are only considered accurate within approximately 100 MPa (due to the assumptions involved, all stresses in the table are rounded to the nearest 100 MPa). The coating-substrate thermal strain range was calculated using the coating and substrate mean CTE values from 25 to 800°C. Coating values were measured on free-standing coatings.[2, 11] The thermal mismatch strain was added (with appropriate sign) to the initial residual stress to obtain the coating stress at 800°C in the first heating cycle assuming no stress relaxation by plastic deformation or creep. Elastic moduli for the coatings used in the calculation were measured on free-standing specimens. If the coatings are assumed to be very weak at 800°C (reasonable for all coatings in these tests), any stresses present during the one hour hold at this temperature can be assumed to relax, either in the first or subsequent cycles, and the coating stress after cooling from this stress-free condition can be calculated from the thermal mismatch strain, as shown in the next-to-last column. The final column of the table shows the test results.

Observation of coating cracking and the number of cycles in which it occurred appears to roughly correlate with the thermal mismatch strain range and the stresses developed in the coating during cycling. Coatings subjected to low thermal strain ranges and stress levels tend not to crack or crack after more cycles, while coatings at higher levels crack severely. Note that in the case of the FeAl coatings, high levels of initial compressive residual stress do not appear to be beneficial, since these are added to the compressive thermal mismatch strain. The influence of substrate is shown by the tests of Fe_3Al coatings on 316 SS and IN 600 substrates. No cracking was observed for 316 SS, which had less thermal mismatch than IN 600, in which some cracking was observed after 30 cycles.

Table 1: Results of thermal cycle tests from 25 to 800°C in an air environment along with simple elastic analysis of coating stresses and thermal mismatch strains.

Case	Initial Residual Stress	CTE Mismatch Thermal Strain Range	Coating Stress at 800°C	Coating Stress at RT (After Relaxation)	Cracking?
FeAl-540-316SS	–100 MPa	0.27%	–400 MPa	+300 MPa	No
FeAl-660-316SS	–200 MPa		–600 MPa	+400 MPa	30 cycles
FeAl-700-316SS	–400 MPa		–800 MPa	+400 MPa	15 cycles
Fe3Al-560-316SS	–100 MPa	0.12%	0 MPa	–100 MPa	No
Fe3Al-620-316SS	–500 MPa		–400 MPa	–100 MPa	No
Fe3Al-560-IN600	0 MPa	0.16%	–100 MPa	+100 MPa	30 cycles
Fe3Al-600-IN600	– 200 MPa		–400 MPa	+200 MPa	1 cycle
Fe3Al-620-IN600	–400 MPa		–600 MPa	+200 MPa	30 cycles
Mo-Si-B-316SS	0 MPa	0.86%	+1400 MPa	–1500 MPa	Yes
316SS-520-316SS	–200 MPa	None	–200 MPa	None	No
316SS-640-316SS	–300 MPa		–300 MPa		

COATING FRACTURE STRAINS

The fracture strain (mean of two measurements) for Fe_3Al coatings applied to 316 SS substrates at a spray particle velocity of 560 m/s was 0.41%; the fracture strain for identical coatings applied at 620 m/s was slightly higher, 0.43%. On low-carbon steel substrates, however, the fracture strain of Fe_3Al coatings applied at 560 m/s was markedly lower, 0.15%. FeAl coatings were slightly less ductile than the Fe_3Al coatings—the fracture strains on 316 SS substrates at spray particle velocities of 540 and 700 m/s were 0.31 and 0.26%, respectively. With the exception of the Fe_3Al coating applied to low-carbon steel, the coating fracture strains exceeded the yield strain of the substrates, which were 0.13% for low-carbon steel and 0.15% for 316 SS. Hence the coatings would be expected to withstand cracking at room temperature for reasonable load levels, but would be cracked by cold-forming operations which involve significant plastic strain. The differences between the coating materials agrees with the generally more brittle nature of FeAl compared to Fe_3Al.[12, 13] The marked reduction in fracture strain for low-carbon steel likely arises from the difference in coating residual stress in comparison with that found when applied to 316 SS. While a compressive stress of approximately 150 MPa is found on 316 SS, essentially no residual stress exists on low-carbon steel. The presence of the compressive residual stress increases the net observed fracture strain for Fe_3Al when measured on 316 SS. The residual stress differences for the two substrate materials arise from the difference in substrate CTE when cooling from the coating deposition process.

CONCLUSIONS

The coating performance tests performed to date have included TGA testing of free-standing coatings in a simulated coal combustion gas environment, thermal cycling tests of coated substrates, and coating fracture strain measurements at room temperature. The iron aluminide coatings (both Fe_3Al and FeAl) tested have shown good resistance to gas-phase corrosion. Corrosion rates for the coatings were slightly greater than wrought Fe_3Al, which was essentially impervious, and were much lower than rates measured for typical substrate materials. No disernable effect of coating type, spray parameters, or test temperature was observed within the range of 500 to 800°C. Resistance to cracking and coating debonding during thermal cycling appeared to be mainly linked to the mismatch in CTE between the coating and the substrate, with initial residual stress level playing a secondary role. Iron aluminide coatings applied to 316 SS substrates showed reasonable strains to fracture at room temperature, 0.3 to 0.4%. These strains were well in excess of the substrate yield strains. Due to a difference in residual stress, the fracture strain of a Fe_3Al coating applied to a low-carbon steel substrate was considerably lower, 0.13%.

ACKNOWLEDGEMENTS

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